

***Modeling Expected Solute Concentration in Randomly Heterogeneous Flow Systems with Multi-Component Reactions***

By Maria E. Malmström, Georgia Destouni, and Philippe Martinet

**Appendix 1. PHREEQC implementation of base-case model scenarios.** The geochemical model scenarios were implemented using the PHREEQC model (1) in conjunction with the PHREEQC database (2) for speciation and solubility equilibria. Calcite was the only original mineral in the groundwater system that was assumed to dissolve, and its initial concentration was arbitrarily set to 0.3 moles per liter of soil solution, corresponding to ~0.5 vol.-% of the solids. The carbon dioxide partial pressure in Henry's law's equilibrium with the groundwater was set at the atmospheric level,  $P_{CO_2} = 3 \times 10^{-4}$  atm.

The groundwater was assumed to be anoxic and non-reducing, therefore, no reactions involving dissolved molecular oxygen or organic components were modeled. The initial groundwater was, as a conservative estimate, taken as pure water with a sulfuric acid acidity of  $2 \times 10^{-5}$  M. The composition of the incoming impoundment water was assumed to be constant over time with concentrations of dissolved components as listed in Table 1. For the simplified reaction system in scenario A, the groundwater as well as the impoundment water was modeled as a buffer solution containing 1.0 M  $NaHCO_3$ , thereby maintaining pH at 6.5 throughout the simulations.

Secondary minerals that were allowed to precipitate and potentially redissolve were amorphous aluminum hydroxide, gypsum, and siderite. In Scenario B, also smithsonite was considered. In scenario A, hydrous ferric oxide (HFO) with a surface site concentration of 0.01 moles per liter of soil solution was acting as a sorbent for  $Zn^{2+}$ . Sorption of  $Zn^{2+}$  and acid base properties of the HFO was modeled using surface complexes as listed in Table Supp-1 without correction for electrostatic interactions at the surface. The temperature was set to 4°C in all simulations.

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**Table Supp-1.** Surface speciation model for HFO in model scenario A.

Surface reaction	Equilibrium constant <sup>#</sup>
$\equiv\text{FeOH}_2^+ \leftrightarrow \equiv\text{FeOH} + \text{H}^+$	$\log K_{a1} = -7.0$
$\equiv\text{FeOH} \leftrightarrow \equiv\text{FeO}^- + \text{H}^+$	$\log K_{a2} = -8.8$
$\equiv\text{FeOH} + \text{Zn}^{2+} \leftrightarrow \equiv\text{FeOZn}^+ + \text{H}^+$	$\log K_{=\text{FeOZn}^+} = 1.0$

<sup>#</sup>Equilibrium constants for strong sorption sites from Dzombak and Morel (3). Weak sites were not considered, however, the choice of strong/weak sites was not critical to our model results.

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**Appendix 2. Mathematical definition of simplified reaction system.** We assess a simplified reaction system in which we only consider simplified aqueous speciation of components and attenuation of  $Zn^{2+}$  through sorption at a constant pH of 6.5. For the analytical solution, the sorption reaction is quantified through an isotherm, such that the sorbed concentration of  $Zn^{2+}$ ,  $N_{Zn^{2+}}$ , relates to the free, aqueous concentration of  $Zn^{2+}$ ,  $C_{Zn^{2+}}$ , as

$$N_{Zn^{2+}} = \frac{\alpha C_{Zn^{2+}}}{\beta + K_s C_{Zn^{2+}}} \quad (A2-1),$$

in which  $\alpha$ ,  $\beta$ , and  $K_s$  denote sorption isotherm constants. Equation A2-1 equals a Langmuir adsorption isotherm if  $\beta=1$  and  $\alpha=\Gamma_{max}K_s$ , where  $\Gamma_{max}$  is the maximum concentration of sorbed solute; for this case,  $K_s$  is the sorption constant. By combining the surface speciation reactions defined in Table Supp-1 with a mole balance over the surface sites  $\{FeOH\}_{tot} = \{FeOH\} + \{FeOH_2^+\} + \{FeO^-\} + \{FeOZn^+\}$ , where curled brackets refer to surface concentrations, it can be shown that Equation A2-1 is equivalent to the surface complexation model in Table Supp-1 in Appendix 1 in the Supporting Information when  $\alpha = \{FeOH\}_{tot} K_{=FeOZn^+}$ ,  $\beta = \left( [H^+] + \frac{[H^+]}{K_{a1}} + K_{a2} \right)$ , and

$$K_s = K_{=FeOZn^+}.$$

Detailed speciation modeling using the PHREEQC model (1) in conjunction with the PHREEQC database (2) indicated that the speciation of  $Zn^{2+}$  in the aqueous solution is dominated by the free aqua ion and the first two sulfate complexes, such that the total dissolved concentration of  $Zn^{2+}$  can be approximated as

$$C_{Zn^{2+}}^{tot, aq} \approx C_{Zn^{2+}} + C_{ZnSO_4(aq)} + C_{Zn(SO_4)_2^-} \quad (A2-2).$$

This implies that the modeling of  $Zn^{2+}$  transport and attenuation must include quantification of sulfate transport and speciation. Sulfate speciation, in turn, is dominated by the free sulfate ion and complexes with  $Mg^{2+}$  and  $Fe^{2+}$ .

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For the simplified reactions system, dominant species of sulfate are  $SO_4^{2-}$ ,  $FeSO_{4(aq)}$ , and  $MgSO_{4(aq)}$ . The total concentrations of zinc and sulfate can be expressed as

$$C_{Zn^{2+}}^{tot, aq} \approx C_{Zn^{2+}} (1 + K_{ZnSO_{4(aq)}} C_{SO_4^{2-}} + K_{Zn(SO_4)_2^{2-}} C_{SO_4^{2-}}^2) \quad (A2-3)$$

$$C_{SO_4^{2-}}^{tot, aq} \approx C_{SO_4^{2-}} (1 + K_{MgSO_{4(aq)}} \frac{C_{Mg^{2+}}}{1 + C_{SO_4^{2-}}} + K_{FeSO_{4(aq)}} \frac{C_{Fe^{2+}}}{1 + C_{SO_4^{2-}}}) \quad (A2-4)$$

where  $K_i$  denotes the formation constant for species  $i$ . For this study, values of the formation constants were obtained from the PHREEQC database (2). In the simplified model scenario, sulfate, magnesium, and iron are considered not to be attenuated. The coupled, governing Lagrangian transport equations then become

$$\frac{\partial C_{Zn^{2+}}^{tot, aq}}{\partial t} + \frac{\partial C_{Zn^{2+}}^{tot, aq}}{\partial \tau} + \frac{\partial N_{Zn^{2+}}}{\partial t} = 0 \quad (A2-5)$$

$$\frac{\partial C_{SO_4^{2-}}^{tot, aq}}{\partial t} + \frac{\partial C_{SO_4^{2-}}^{tot, aq}}{\partial \tau} = 0 \quad (A2-6)$$

$$\frac{\partial C_{Mg^{2+}}^{tot, aq}}{\partial t} + \frac{\partial C_{Mg^{2+}}^{tot, aq}}{\partial \tau} = 0 \quad (A2-7)$$

$$\frac{\partial C_{Fe^{2+}}^{tot, aq}}{\partial t} + \frac{\partial C_{Fe^{2+}}^{tot, aq}}{\partial \tau} = 0 \quad (A2-8)$$

Equations A2-1 and A2-3 - A2-8, hence, define the simplified, coupled reactive-transport problem. The solution is shown in Appendix 3 in the Supporting Information.

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**Appendix 3. Analytical solution to the simplified reactive transport problem.** The coupled reactive transport problem is defined by Equations A2-1 and A2-3 - A2-8 in Appendix 2 in the Supporting Information.

Equations A2-6 – A2-8 all have the simple solution (e.g., 4):

$$C^{tot, aq}(t, \tau) = C_{in}^{tot, aq} + (C_0^{tot, aq} - C_{in}^{tot, aq})H(t - \tau) \quad (A3-1),$$

where H is the Heaviside step function,  $C_{in}^{tot, aq}$  denotes the total dissolved concentration of the solute in the transport domain at  $t=0$ , and  $C_0^{tot, aq}$  is the concentration of the solute in the inflowing water, i.e.,  $C^{tot, aq} = C_{in}^{tot, aq}$  for  $x>0$ ,  $t=0$  and  $C^{tot, aq} = C_0^{tot, aq}$  for  $x=0$ ,  $t>0$  (compare Figure 1). For our simplified reaction system, Table 1 lists  $C_0^{tot, aq}$ ;  $C_{in}^{tot, aq} = 0$  for all components except sulfate, for which  $C_{in, SO_4}^{tot, aq} = 1 \cdot 10^{-5}$  M.

In order to obtain  $C_{Zn^{2+}}^{tot, aq}(t, \tau)$ , we first insert Equation A2-3 in A2-1 to get

$$N_{Zn^{2+}} = \frac{\alpha \gamma C_{Zn^{2+}}^{tot, aq}}{\beta + K_s \gamma C_{Zn^{2+}}^{tot, aq}} \quad (A3-2),$$

in which  $\gamma(C_{SO_4^{2-}}) = \left[ 1 + K_{ZnSO_4(aq)} C_{SO_4^{2-}} + K_{Zn(SO_4)_2} C_{SO_4^{2-}}^2 \right]^{-1}$ . Because sulfate, iron, and magnesium are not attenuated, they, at any point along the streamline, arrive before  $Zn^{2+}$ . Thus, in solving the coupled Equations A3-2 and A2-5,  $\gamma$  can be considered as constant when sorption occurs; the constant value of  $\gamma = \gamma(C_{SO_4^{2-}}^*)$  is for

$$C_{SO_4^{2-}}^* \text{ as obtained from Equation A2-4 for } t > \tau, C_{0, SO_4^{2-}}^{tot, aq} = C_{SO_4^{2-}}^* \left( 1 + K_{MgSO_4(aq)} \frac{C_{0, Mg^{2+}}^{tot, aq}}{1 + C_{SO_4^{2-}}^*} + K_{FeSO_4(aq)} \frac{C_{0, Fe^{2+}}^{tot, aq}}{1 + C_{SO_4^{2-}}^*} \right).$$

By introduction of  $\gamma$  in Equation A3-2, we expressed the sorption isotherm in terms of the *total dissolved* concentration of  $Zn^{2+}$  and isotherm and speciation constants only; thus, Equation A3-2 can be solved directly in conjunction with the reactive-transport equation, Equation A2-5, without further consideration of the aqueous speciation.

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The solution to the coupled Equations A2-5 and A3-2 is (e.g., 4):

$$C_{Zn^{2+}}^{tot, aq}(t, \tau) = C_{in, Zn^{2+}}^{tot, aq} + \left( C_{0, Zn^{2+}}^{tot, aq} - C_{in, Zn^{2+}}^{tot, aq} \right) H(\tau_s(t) - \tau) \quad (A3-3),$$

where  $C_{Zn^{2+}}^{tot, aq} = C_{in, Zn^{2+}}^{tot, aq}$  for  $x > 0, t = 0$  and  $C_{Zn^{2+}}^{tot, aq} = C_{0, Zn^{2+}}^{tot, aq}$  for  $x = 0, t > 0$ , and where

$$\tau_s = \left[ 1 + \frac{N_0 - N_{in}}{C_{0, Zn^{2+}}^{tot, aq} - C_{in, Zn^{2+}}^{tot, aq}} \right]^{-1} t \quad (A3-4).$$

In Equation A3-4,  $N_{0, Zn^{2+}} = \frac{\alpha \gamma C_{0, Zn^{2+}}^{tot, aq}}{\beta + K_s \gamma C_{0, Zn^{2+}}^{tot, aq}}$  and  $N_{in, Zn^{2+}} = \frac{\alpha \gamma C_{in, Zn^{2+}}^{tot, aq}}{\beta + K_s \gamma C_{in, Zn^{2+}}^{tot, aq}}$  for our sorption isotherm. For our

simplified reaction system,  $N_{in} = C_{in, Zn^{2+}}^{tot, aq} = 0$ .

### **References**

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